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(54) **ADHESIFS THERMODURCISSABLES ET SANS SOLVANT AYANT UN CONSTITIANT A BASE DE POLYURETHANES ET LESQUELS NE DONNENT PAS DE PRODUITS D'ELIMINATION ETLEUR UTILISATION**

(54) **HEAT-CURING SOLVENT-FREE ONE-COMPONENT ADHESIVE WHICH IS BASED ON POLYURETHANES AND WHICH DOES NOT GIVE OFF ELIMINATION PRODUCTS, AND ITS USE**

(57) TRANSLATION NOT AVAILABLE AT THIS TIME

(57) Disclosed is a composition comprising: A) as a hardener component, a polyaddition product containing hydroxyl and uretdione groups, B) as a binder component, a hydroxyl-containing compound, and, C) optionally auxiliaries and additives. Also disclosed is the preparation of the composition and its use as a heat-curing, one-component, solvent-free polyurethane (PU) adhesive which does not give off elimination products.

ABSTRACT OF THE DISCLOSURE

Disclosed is a composition comprising:

A) as a hardener component, a polyaddition product containing hydroxyl and uretdione groups,

B) as a binder component, a hydroxyl-containing compound, and,

C) optionally auxiliaries and additives. Also disclosed is the preparation of the composition and its use as a heat-curing, one-component, solvent-free polyurethane (PU) adhesive which does not give off elimination products.

Heat-curing solvent-free one-component adhesive which is based on polyurethanes and which does not give off elimination products, and its use

The invention relates to the use of polyaddition products containing hydroxyl and uretdione groups to prepare heat-curing solvent-free one-pack compositions which do not give off elimination products upon curing and are useful as adhesives.

Polyurethane adhesives are generally notable for very good properties of adhesion to surfaces of a very wide range of materials, for resistance to solvents, plasticizers, fats, oils and water, and for the high flexibility of the adhesive films even at low temperatures. Owing to the great variety of polyurethane chemistry, the literature - see e.g. G. Habenicht, Kleben - Grundlagen, Technologie, Anwendungen [Bonding - principles, technology, applications], Springer Verlag, Berlin, Heidelberg, New York, Tokyo, 1986 - recognizes a number of different types of polyurethane adhesives. A distinction is made between one-component ("one-pack or one-can") and two-component ("two-pack or two-can") systems. Two-pack polyurethane adhesives are essentially characterized by polyisocyanates as hardeners and by predominantly oligomeric diols and/or polyols as resin. They have the advantage of presenting no great problems in terms of shelf life and that by a skillful choice and targeted reactivity of the monomers it is possible to formulate systems having different pot lives and adhesive-film-determining properties, for example strength, elasticity and resistance to chemicals. Owing to

polyaddition reactions, these adhesives do not release any elimination products in the course of crosslinking.

The technical effort required when processing two-pack systems in terms of

precise dosing and mixing of the components has led to the development of one-pack systems, which are easier to process. These contain isocyanato prepolymers which are prepared from polyols of relatively high molecular mass with a stoichiometric excess of polyisocyanate. Full curing takes place in most cases through moisture-induced crosslinking. For this reason, sufficient atmospheric humidity (at least 40% rel. humidity) in the processing areas is required. Consequently, these adhesives are of only limited usefulness for bonds where the parts to be joined are metallic or otherwise moisture-impermeable. Owing to the exclusion of moisture, the packaging of these one-pack adhesives during transportation and storage is critical.

A further development comprises the aftercrosslinking polyurethane hot-melt adhesives (reactive hot melts) which following application from the melt provide, after cooling (physically setting), a spontaneous initial strength and subsequently react, under the action of further ambient atmospheric humidity on the remaining reactive isocyanate groups, to form the adhesive-film polymer.

In the case of the crosslinking reaction by means of moisture, the formation of carbon dioxide as a result of the breakdown of the unstable carbamic acid derivatives may be critical, especially when relatively thick adhesive films of relatively high viscosity are present and when the gas bubbles are enclosed in the adhesive film. Moreover, moisture-curing PU adhesives do not attain the strengths of two-pack PU adhesives.

An alternative to the moisture-curing systems is represented by one-pack heat-activatable PU adhesives. These consist of polyol resins and of polyisocyanates whose isocyanate groups are inhibited by so-called blocking agents. Elevated temperatures lead to cleavage of the hardener molecules, in the course of which the blocking agents are eliminated and the polymer is generated by polyurethane formation. Here too, a disadvantage is the formation of elimination products in the sense of the adverse effect this has on the adhesion properties. Moreover, the organic structure of some blocking agents renders them toxicologically unacceptable.

Polyurethanes are likewise employed as solvent-containing adhesive systems. In this case, a distinction may be made between physically setting and chemically reacting systems. Both systems possess high molecular mass hydroxy polyurethanes as polymers, while the chemically reacting systems additionally include a polyisocyanate as second component in the solvent system. In order to form the adhesive film, a process which may take place at normal or elevated temperature, it is necessary to remove the solvent.

However, the interests of environmental protection and adhesive technology make it desirable to provide adhesives which are free from emissions in the form of solvent or of elimination products, such as blocking agents.

A major object on which the invention is based, therefore, is to develop new PU adhesives unhampered by the above-mentioned disadvantages of the prior art. In other words, they should be one-pack systems free from blocking agents and solvents and should be able to be crosslinked thermally to form thermosets.

The text below describes the novel binder/hardener mixture in which curing agents are polyaddition products containing hydroxyl and uretdione groups.

In one broad aspect, the present invention therefore provides a heat-curing one-component solvent-free composition which does not give off elimination products upon curing. The composition comprises:

A) as a hardener component, a polyaddition product containing a free hydroxyl group and an internal uretdione

group, and

B) as a binder component, a compound containing a hydroxyl group, and

C) optionally auxiliaries and additives.

The hardener component A) is obtainable by reacting

(i) a uretdione-containing compound based on a polyisocyanate, preferably an aliphatic and/or cycloaliphatic diisocyanate having at least two free isocyanate groups, and

(ii) an isocyanate-reactive difunctional compound optionally together with an isocyanate-reactive monofunctional compound, preferably a simple diol or chain extender, optionally together with a monoalcohol or monoamine,

where the polyaddition product which contains a uretdione group can be prepared either in a solvent or without a solvent, preferably without a solvent.

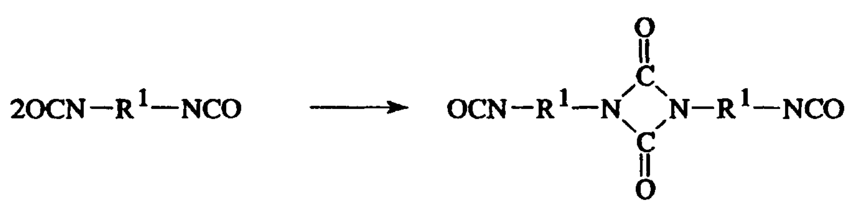
The binder component B) consists of a hydroxyl-containing compound having a molecular weight of at least 60, an OH number of at least 20 mg of KOH/g and a hydroxyl functionality of at least 2.

The mixing ratio of the hydroxyl-containing compound B) to the polyaddition product containing hydroxyl and uretdione groups (crosslinker) A) is generally chosen such that there is from about 0.5 to about 1.2, preferably from 0.8 to 1.1, very particularly preferably 1.0, NCO group per OH group.

The invention additionally provides a process for preparing the heat-curing one-component solvent-free composition.

The invention also provides for the use of the novel heat-curing one-component solvent-free composition for the bonding of any desired heat-resistant substrate, especially for the bonding of a metal.

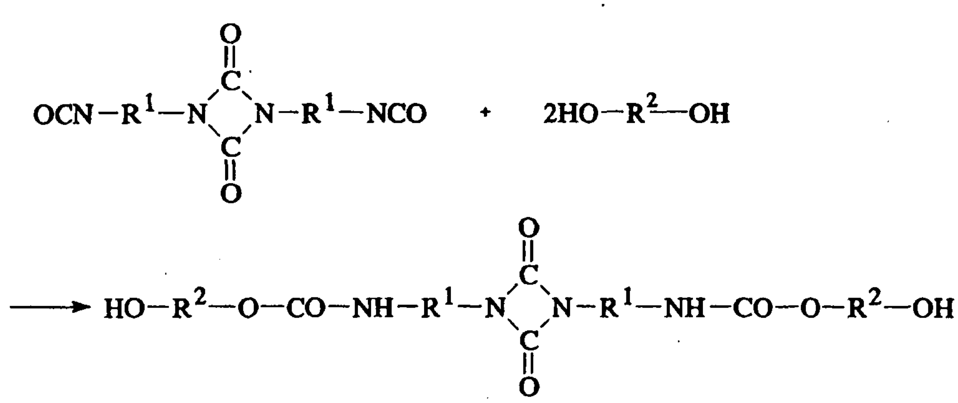
The hardener component A) comprises a polyaddition compound which carry a uretdione group. The uretdione product, which in addition to the uretdione may also contain up to 40% by weight of a trimer, and higher oligomers, is based on the reaction product of the dimerization of a polyisocyanate, preferably on the dimerization product of an aliphatic and/or cycloaliphatic diisocyanate. Examples of the diisocyanates which are employed include 1,6-diisocyanatohexane (HDI), 2-methyl-1,5-diisocyanatopentane (MPDI), 2,2,4- and 2,4,4-trimethyldiisocyanatohexane (TMDI), 1-isocyanato-3-isocyanatomethyl-3,5,5-trimethylcyclohexane (IPDI) and 4,4'-diisocyanatodicyclohexylmethane ($H_{12}MDI$) or any desired mixtures of these diisocyanates. The dimerization of a diisocyanate is believed to proceed typically according to the following reaction scheme:



wherein R^1 is the residue of the diisocyanate.

The preparation of the polyaddition compound of this kind containing an internal uretdione group and terminal hydroxyl groups by a reaction of the uretdione-group-

containing polyisocyanate with an isocyanato-reactive difunctional compound optionally together with an isocyanate-reactive monofunctional compound, preferably a diol and/or chain extender, optionally together with a monoalcohol or monoamine, is known in principle and is described, for example, in DE-C 24 20 475, DE-C 30 30 572, DE-C 30 30 588, DE-C 30 30 539, EP-B 0 669 353 and EP-B 0 669 354. This reaction is believed to typically proceed according to the following reaction scheme:



wherein R^2 is the residue of the diol or chain extender. The "diols" are those relatively simple diols among those "polyols" described hereinunder as examples of the binder components C). The "chain extenders" include polyether diols, polyester diols and the like also described hereinunder as examples of the binder components C). The polyaddition compounds containing uretdione groups which are used as hardeners generally have an overall NCO content of from about 3 to about 26% (determined by heating the compounds at 180°C for from 30 to 60 minutes). This "hot value" is a direct

measure of the content of uretdione groups in the reaction product. The melting point of these compounds is generally in the range from 40 to 130°C. The polyaddition compounds have substantially no free isocyanate groups but have internal uretdione groups which are considered as a latent form of NCO groups. The overall (or total) NCO content mentioned above is therefor practically the content of the uretdione groups.

Preferred binder components B) are compounds containing functional groups which in the course of the curing process can react with isocyanate groups as a function of temperature and time. These functional groups include at least one hydroxyl group and may additionally include carboxyl, mercapto, amino, urethane and (thio)urea groups. As polymers it is possible to employ additional polymers, condensation polymers and polyaddition compounds.

Preferred components are primarily polyethers, polythioethers, polyacetals, polyesteramides, amino resins and their modification products with polyfunctional alcohols, polyazomethines, polysulfonamides, acrylate resins, melamine derivatives, cellulose esters and cellulose ethers, and polyureas, but especially simple polyols, polyesters and polyurethanes.

Examples of preferred simple polyols are those generally having up to about 20 carbon atoms including ethylene glycol, propylene 1,2- and 1,3-glycol, butylene 1,4- and 2,3-glycol, di-β-hydroxybutanediol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,12-dodecanediol, 1,18-octadecanediol, neopentylglycol, cyclohexanediol, bis(1,4-

hydroxymethyl)cyclohexane, 2,2-bis(4-hydroxycyclohexyl)-propane, 2,2-bis[4-(β-hydroxyethoxy)phenyl]-propane, 2-methyl-1,3-propanediol, 2-methyl-1,5-pentanediol, 2,2,4- and 2,4,4-trimethyl-1,6-hexanediol, glycerol, 1,1,1-trimethylolpropane, 1,1,1-trimethylolethane, 1,2,6-hexanetriol, 1,2,4-butanetriol, tris(β-hydroxyethyl) isocyanurate, pentaerythritol, mannitol, sorbitol and also diethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol, polypropylene glycols, polybutylene glycols, xylylene glycols and neopentylglycol hydroxypivalate. It is of course also possible to employ mixtures of two or more polyhydroxy compounds.

Carboxylic acids which are preferred for the preparation of polyesters may be aliphatic, cycloaliphatic, aromatic and/or heterocyclic in nature and may optionally be substituted by halogen atoms and/or unsaturated. Examples of these acids which may be mentioned are succinic, adipic, suberic, azelaic, sebacic, phthalic, terephthalic, isophthalic, trimellitic, pyromellitic, tetrahydrophthalic, hexahydrophthalic, hexahydroterephthalic, di- and tetrachlorophthalic, endomethylenetetrahydrophthalic, dodecanedioic, dimeric fatty, glutaric, maleic and fumaric acids and, where obtainable, their anhydrides, dimethyl terephthalate and bisglycol terephthalate.

Preferred polyhydric alcohol components for preparing the polyesters are the polyols mentioned above by way of example. Such compounds which are made by reaction of carboxylic acids and polyols have terminal hydroxyl groups and are called as polyester polyols.

Polyesters of lactones or hydroxycarboxylic acids may likewise be employed.

When preparing the polyester polyols it is of course possible to employ any desired mixtures of the carboxylic acids mentioned by way of example and/or their anhydrides or esters, or any desired mixtures of the exemplified polyhydric alcohols.

For the purposes of the invention, polyester polyols as the binder component B) may preferably consist of two types having different characteristics. Preferred polyester polyols of type I have an OH functionality of from 2.0 to 5.0, preferably from 2.0 to 4.0, an OH number of from 20 to 200 mg of KOH/g, preferably from 30 to 150 mg of KOH/g, a molecular weight of from 1500 to 30,000, preferably from 2000 to 7000, a viscosity at 130°C of <300,000 mPa·s, a melting point or flow point of up to about 230°C, and a glass transition temperature (T_g) of from -80 to 120°C. The morphology of the polyesters ranges from amorphous to crystalline. Preferred polyester polyols of types II have an OH functionality of from 2.0 to 5.0, an OH number of from 100 to 600 mg of KOH/g, preferably from 100 to 400 mg of KOH/g, and a molecular weight of from 100 to 2000.

The polyester polyols of both types may also possess acid numbers of up to about 35 mg of KOH/g.

The polyester polyols can be obtained in a known manner by condensation in an inert gas atmosphere at temperatures from 100 to 260°C, preferably from 130 to 220°C, in the melt or by an azeotropic procedure, as is described, for

example, in Houben-Weyl, Methoden der Organischen Chemie, Vol. 14/2, 1-5, 21, 23, 40, 44, Georg Thieme Verlag, Stuttgart, 1963 or in C.R. Martens, Alkyd Resins, 51-59, Reinhold Plastics Appl. Series, Reinhold Publishing Comp., New York, 1961.

The polyurethane polyols are reaction products of

(i) a polyisocyanate component consisting of at least one organic polyisocyanate, with

(ii) a polyol component consisting of at least one di- to hexahydric alcohol which may contain ester, ether and/or acrylate linkages.

Preferred polyisocyanates (i) include both aromatic and, in particular, (cyclo)aliphatic diisocyanates, such as 1,6-diisocyanatohexane (HDI), 2-methyl-1,5-diisocyanatopentane (MPDI), 2,2,4- and 2,4,4-trimethyldiisocyanatohexane (TMDI), 1-isocyanato-3-isocyanatomethyl-3,5,5-trimethylcyclohexane (IPDI) and 4,4'-diisocyanatodicyclohexylmethane ($H_{12}MDI$). Also possible is molecular enlargement of the polyisocyanates mentioned by way of example. The molecular enlargement may be accomplished by dimerization, trimerization, carbodiimidization, allophanate formation and biuretization, as is described, for example, in DE-A 29 29 150. In the preparation of the polyurethane polyols, it is of course possible to employ any desired mixtures of the polyisocyanates mentioned by way of example.

Typical examples of polyhydric alcohols (ii) without additional functional groups are, for example, ethylene glycol, propylene 1,2- and 1,3-glycol, butylene 1,4- and 2,3-

glycol, di-β-hydroxybutanediol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,12-dodecanediol, 1,18-octadecanediol, neopentylglycol, cyclohexanediol, 1,4-bis(hydroxymethyl)cyclohexane, 2,2-bis(4-hydroxycyclohexyl)propane, 2,2-bis[4-(β-hydroxyethoxy)phenyl]propane, 2-methyl-1,3-propanediol, 2-methyl-1,5-pentanediol, 2,2,4- and 2,4,4-trimethyl-1,6-hexanediol, glycerol, 1,1,1-trimethylolpropane, 1,1,1-trimethylolethane, 1,2,6-hexanetriol, 1,2,4-butanetriol, tris(β-hydroxyethyl)isocyanurate, pentaerythritol, mannitol, sorbitol and also diethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol, polypropylene glycols, polybutylene glycols, xylylene glycols and neopentylglycol hydroxypivalate. Preferably, those polyols have 2 to 6 hydroxyl groups and up to about 20 carbon atoms. It is of course also possible to employ mixtures of two or more polyhydroxy compounds.

Examples of preferred polyester polyols (ii) are, in particular, the reaction products, which are known *per se* in polyurethane chemistry, of polyhydric alcohols of the above-mentioned type with polycarboxylic acids. Suitable polycarboxylic acids may be aliphatic, cycloaliphatic, aromatic and/or heterocyclic in nature and may optionally be substituted by halogen atoms and/or unsaturated. Examples of these acids which may be mentioned are succinic, adipic, suberic, azelaic, sebacic, phthalic, terephthalic, isophthalic, trimellitic, pyromellitic, tetrahydrophthalic, hexahydrophthalic, hexahydroterephthalic, di- and tetrachlorophthalic, endomethylenetetrahydrophthalic, dodecanedioic, dimeric fatty,

glutaric, maleic and fumaric acids and, where obtainable, their anhydrides, dimethyl terephthalate and bis-glycol terephthalate. Polyesters in the form of lactones or hydroxycarboxylic acids can likewise be employed. For the preparation of the polyesterpolyols, it is of course possible to employ any desired mixtures of the polyhydric alcohols mentioned by way of example or any desired mixtures of the carboxylic acids mentioned by way of example, and/or their anhydrides or esters.

Preferred polyether polyols (ii) are the ethoxylation and/or propoxylation products, known per se from polyurethane chemistry, of appropriate divalent to tetravalent starter molecules, for example water, ethylene glycol, propylene 1,2- and 1,3-glycol, 1,1,1-trimethylolpropane, glycerol and/or pentaerythritol.

Preferred polyhydroxypolyacrylates (ii) comprise copolymers, known per se , of simple esters of acrylic acid and/or methacrylic acid and optionally styrene, with hydroxyalkyl esters of these acids being used in order to introduce the hydroxyl groups, examples of such esters being the 2-hydroxyethyl, 2-hydroxypropyl and 2-, 3- and 4-hydroxybutyl esters.

Preferred polyhydroxypolyesters as described above, polyhydroxypolyethers and polyhydroxypolyacrylates generally have a hydroxyl number of from 20 to 200 mg of KOH/g, preferably from 50 to 130 mg of KOH/g, based on 100% products.

The polyurethane polyols are preferably prepared in inert solvents, for example ketones, at temperatures from 20

to 90°C. In this context the amounts of the reactants generally correspond to an NCO/OH ratio of from 1:1.4 to 1:15.

The polyols, polyester polyols and polyurethane polyols mentioned by way of example can be mixed with one another in any desired proportions and can be reacted with the hardener component A).

In the course of the preparation of the novel adhesives it is possible, if required, to add additives and auxiliaries which are customary in the adhesive sector, such as catalysts, adhesion promoters, adhesive resins, leveling agents, fillers, pigments, dyes, UV stabilizers and antioxidants. The catalysts are preferably organotin compounds and may be used in a concentration of 0.01 to 1%, preferably 0.01 to 0.5% by weight based on the composition.

For the preparation of the novel PU adhesives, the hardener component A) is either homogenized in an inert solvent, for example acetone, or after milling is mixed and homogenized in the melt, in both cases together with the hydroxyl-containing polymers B) and optionally with catalysts and also with further auxiliaries and additives. In the case of homogenization in a solvent, the solvent is removed, preferably by distillation in vacuo. The resulting product may then be ground using a mill to a particle size of less than 500 µm. Homogenization in the melt can take place in suitable apparatus, for example extruders or heatable compounders, but preferably by extruding in a twin-screw extruder, in the course of which an upper temperature limit of 180°C, preferably 150°C, should not be exceeded. The

compounded or extruded mass is cooled to room temperature, comminuted appropriately and ground using a mill to less than 500 μm.

Application of the one-component adhesive to the substrates which are to be bonded may take place, for example, by electrostatic powder spraying, fluidized-bed sintering, electrostatic fluidized-bed sintering, melting or sieving. Following application of the novel adhesive formulation to the clean surfaces of the parts to be joined, the bond is fixed optionally, for example by means of appropriate tools or a weight. Curing of the coated workpieces takes place at from 150 to 220°C over a sufficient period of time, for example, from 60 to 4 minutes, preferably at from 160 to 200°C over a period of from 30 to 6 minutes.

The novel resin/hardener systems can be employed, for example, as coating compositions for various substrates or, preferably, as adhesive, especially as one-pack PU adhesives for bonding a wide variety of materials, for example metals, light metals, but also nonmetallic materials, such as glass, ceramic or plastic. The substrates used must be resistant to heat.

The novel heat-curing PU adhesives give rise to bonds of excellent tensile

shear strength coupled with adjustable flexibility. The adhesives are extremely advantageous from an ecological viewpoint since they are solvent-free and do not release elimination products in the course of curing.

The subject-matter of the invention is illustrated in more detail below with reference to examples.

The abbreviations used in the examples have the following meanings:

Aa = Adipic acid
DMPA = Dimethylolpropionic acid
EG = Ethylene glycol
HD = 1,6-Hexanediol
IPA = Isophthalic acid
NPG = Neopentylglycol (2,2-dimethyl-1,3-propanediol)
P = 1,5-Pentanediol
PA = Phthalic anhydride
TMA = Trimellitic anhydride
TMHD = Trimethylhexanediol
TMP = 1,1,1-Trimethylolpropane
TPA = Terephthalic acid

A) Preparation of the polyaddition products containing hydroxyl and uretdione groups

The polyaddition products containing hydroxyl and uretdione groups are produced by a known method. The physical and chemical characteristics of the compounds used as hardeners, and the molar compositions thereof, are summarized in Table 1.

The IPDI-uretdione prepared by a known method as an example of uretdiones has the following NCO contents:

free:	16.8 to 18.5 % by weight
total:	37.5 to 37.8 % by weight

The chain extender given by way of example, produced from 1 mol of adipic acid and 2 mol of neopentylglycol, has an OH number of 335 ± 15 mg of KOH/g and a viscosity at 25°C of about 1500 mPa·s.

Table 1: Composition of polyaddition products containing hydroxyl and uretdione groups

Example	Composition [mol]			Chemical and physical characteristics			
	IPDI uretdione	Diols	Chain extender	NCO content [% by weight]		Melting range [°C]	Glass transition temperature [°C]
				free	total		
A) 1	7	6.75 P	1.25 Aa/NPG	< 0.1	13.3	104 - 115	85
A) 2	4	-	5 Aa/NPG	0	9.3	71 - 74	37

B) Hydroxyl-containing compounds

Table 2 below gives an overview of the polyols, hydroxyl-containing polyesters and polyurethanes used to formulate PU adhesives.

Table 2: Hydroxyl-containing compounds used

Example	Manufacturer/Country	Name	Chemical and physical characteristics				
			OH number [mg of KOH/g]	Acid number [mg of KOH/g]	Melting range [°C]	Glass transition temperature [°C]	Viscosity [mPas]
B) 1	Huls/FRG	DYNACOLL® 7130 6)	31 - 39	< 2	-	ca. +30	30,000 (130°C)
B) 2	Huls/FRG	DYNACOLL® 7230 6)	27 - 34	< 2	-	ca. -30	ca.10,000 (80°C)
B) 3	Huls/FRG	DYNACOLL® 7360 6)	27 - 34	< 2	60	ca. -60	ca. 2 000 (80°C)
B) 4	Hüls/FRG	Adhesive resin LTH 7)	ca. 25	12 - 20	90 - 102	-	n.d.
B) 5	Hüls/FRG	Adhesive resin LTW 7)	ca. 30	20 - 30	n.d.	-	n.d.
B) 6	Hüls/FRG	Polyesterpolyol 1[1]	265	1	-	-	n.d.
B) 7	Huls/FRG	Polyesterpolyol 2[2]	104	< 1	-	n.d.	1 200 (160°C)
B) 8	Huls/FRG	Polyesterpolyol 3[3]	103 - 106	25	-	n.d.	n.d.
B) 9	Huls/FRG	Polyurethanepolyol1[4]	76	15	-	n.d.	n.d.
B) 10	Huls/FRG	Polyesterpolyol 4[5]	53	< 1	-	24	n.d.
B) 11	Solvay/FRG	Capa 305 8)	310	< 0.75	0 - 10	n.d.	n.d.
B) 12	Merck/FRG	TMP	1 240	0	56 - 59	n.d.	n.d.

1) Aa/PA/NPG/TMP (0.3:0.7:1.2:0.4),

2) IPA/HD/TMP/TMHD (7:5:2:1),

3) IPA/TMA/HD/TMP/TMHD (6.4:0.9:5.9:1.7:1.0);

4) IPDI/trimers IPDI/TMP/DMPA/PES (Aa/NPG/HD: 4:3:2) (2:1:2:1:2),

5) IPA/TPA/Aa/EG/NPG/TMP (0.3:0.5:0.2:0.6:0.5:0.1); the molar compositions are in brackets; n.d.: not determined,

6) DYNACOLL® 7130, 7230 and 7360 are linear, saturated polyester polyols,

7) LTH and LTW are polyester resins with hydroxyl and carboxyl groups,

8) Capa 305 is a trade-mark for a trifunctional polycaprolactone with terminal hydroxyl groups.

C) Polyurethane adhesives

General preparation procedure for the novel adhesives in solvent

The polyaddition products containing hydroxyl and uretdione groups, hydroxyl-containing compounds and optionally catalysts, auxiliaries and additives are dissolved in an inert solvent such as, for example, acetone. After a homogeneous solution has been obtained, the solvent is removed in vacuo, the solid is comminuted and the comminuted solid is ground in a mill to a particle size <500 μm. This is followed by drying of the substance to constant weight.

General preparation procedure for the novel adhesives in the melt

Hardeners and resins - together if desired with catalyst, auxiliaries and additives - are kneaded in a plastograph at from 70 to 130°C. The cooled mixture of solids is subsequently ground to a particle size <500 μm.

In the case of homogenization in an extruder, the polyaddition compounds containing hydroxyl and uretdione groups are fed into the intake barrel of a twin-screw extruder which is at a temperature of 25 to 170°C, the polyol component at a temperature of 25 to 170°C being metered in simultaneously. The uretdione or the polyol component includes, if appropriate, the required quantity of catalyst, based on the end product.

The extruder used is composed of ten barrels which can be put under

individual thermal control by way of five heating zones. The temperatures of the heating zones are within a large temperature range from 50 to 180°. All temperatures are intended temperatures, and regulation in the barrels takes place by means of electrical heating and pneumatic cooling. The die element is heated by means of an oil thermostat. The speed of rotation of the twin screws, fitted with conveying and, optionally, kneeding elements, is between 50 and 380 rpm.

The mixture is obtained at a rate of from 1 to 130 kg/h. It is either cooled, then comminuted or shaped and bagged, or the actual melt is shaped, cooled and bagged. The fractionated extrudate is ground in a mill to a particle size < 500 µm.

Application of novel adhesives

The novel adhesive formulations are applied from the melt to degreased and roughened standard steel panels (St 1405).

Alternatives to this are sieving the compounds, electrostatic powder spraying, fluidized-bed sintering and electrostatic fluidized-bed sintering.

The bonds are produced in accordance with DIN EN 1465. The tensile shear strengths of these metal bonds, cured at different temperatures in a convection oven, are listed in Table 3.

Table 3: Metal bonds (DIN EN 1465) with the novel hardener/resin mixtures

Example / Formulation	C)1	C)2	C)3	C)4	C)5	C)6	C)7	C)8	C)9	C)10	C)11	C)12	C)13	C)14	C)15	C)16	C)17	C)18	C)19
Hardener A) 1[g]	16.7	31.2	34.9	-	32.1	-	37.2	36.6	-	65.0	-	38.3	39.9	36.5	38.9	64.8	22.7	34.4	19.2
Hardener A) 2[g]	-	-	-	39.8	-	37.4	-	-	48.5	-	73.3	-	-	-	-	-	-	-	-
Polyol acc. to B) 1[g]	83.3	16.5	46.9	43.2	48.9	45.0	47.1	-	-	-	-	-	-	-	-	-	-	-	40.4
Polyol acc. to B) 2[g]	-	16.5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Polyol acc. to B) 3[g]	-	16.5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Polyol acc. to B) 4[g]	-	6.9	6.5	6.0	-	6.3	-	-	-	-	-	-	6.0	-	-	-	-	-	-
Polyol acc. to B) 5[g]	-	-	-	-	6.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Polyol acc. to B) 6[g]	-	-	-	-	-	11.3	15.7	9.5	11.6	-	-	2.7	5.4	-	-	-	-	13.1	-

Table 3: Metal bonds (DIN EN 1465) with the novel hardener/resin mixtures

Example / Formulation	C)1	C)2	C)3	C)4	C)5	C)6	C)7	C)8	C)9	C)10	C)11	C)12	C)13	C)14	C)15	C)16	C)17	C)18	C)19
Polyol acc.B) 7[g]	-	-	-	-	-	-	-	-	-	-	-	-	48.7	63.5	-	-	-	-	-
Polyol acc.B) 8[g]	-	-										59.0	-	-	63.1	28.1			
Polyol acc.B) 9[g]	-	-	-	-	-	-	-	53.9	39.9	27.1	20.7	-	-	-	-	-	-	-	-
Polyol acc.B) 10[g]	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	77.3	52.5	40.4
Polyol acc.B) 11[g]		12.4	11.7	11.0	12.2	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Polyol acc.B) 12[g]		-	-	-	-	-	-	-	-	7.9	6.0	-	-	-	-	7.1			
Tensile shear strength [N/mm²] at 23°C	16	12	25	19	19	18	22	27	20	20	23	24	20	21	22	17	23	23	20
Notes:	OH/NCO ratio = 1:1; curing conditions: 200°C/20 minutes or 180°C/20 minutes																		

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THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A heat-curing one-pack solvent-free composition, which comprises:

A) as a hardener component, a polyaddition product which is derived from a polyisocyanate compound and which has substantially no free isocyanate group but has at least one free hydroxyl group, at least one internal uretdione group and a total NCO content of from about 3 to about 26 wt.%; and,

B) as a binder component, a hydroxy-containing compound having a molecular weight of at least 60, an OH value of at least 20 mg of KOH/g and a hydroxyl functionality of at least 2,

wherein the components A) and B) are contained in such amounts that there is from about 0.5 to about 1.2 NCO group per OH group.

2. A composition as claimed in claim 1, wherein the hardener component A) is obtained by reacting (i) a uretdione-containing compound based on a polyisocyanate having at least two free isocyanate groups and (ii) an isocyanate-reactive difunctional compound alone or together with an isocyanate-reactive monofunctioal compound.

3. A composition as claimed in claim 2, wherein the component (ii) is at least one difunctional member selected from the group consisting of a simple diol and a chain-

extender, alone or together with a monoalcohol or monoamine.

4. A composition as claimed in claim 2, wherein the component (ii) is a simple diol.

5. A composition as claimed in claim 2, wherein the component (ii) is a chain extender selected from the group consisting of a polyether diol and a polyester diol.

6. A composition as claimed in any one of claims 2 to 5, wherein an aliphatic or cycloaliphatic diisocyanate is employed as the polyisocyanate for preparing the hardener component A).

7. A composition as claimed in any one of claims 2 to 5, wherein isophorone diisocyanate (IPDI) is used as the polyisocyanate for preparing the hardener component A).

8. A composition as claimed in any one of claims 1 to 7, wherein the hydroxy-containing compound as the binder component B) is at least one member selected from the group consisting of a simple polyol, a polyester polyol and a polyurethane polyol.

9. A composition as claimed in claim 8, wherein the hydroxy-containing compound as the binder component B) is a simple polyol selected from the group consisting of ethylene glycol, propylene 1,2- or 1,3-glycol, butylene 1,4- or 2,3-

glycol, di-β-hydroxybutanediol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,12-dodecanediol, 1,18-octanediol, neopentylgylcol, cyclohexanediol, 1,4-bis(hydroxymethyl)cyclohexane, 2,2-bis(4-hydroxycyclohexyl)-propane, 2,2-bis[4-(β-hydroxyethoxy)phenyl]propane, 2-methyl-1,3-propanediol, 2-methyl-1,5-propanediol, 2,2,4- or 2,4,4-trimethyl-1,6-hexanediol, glycerol, 1,1,1-trimethylolpropane, 1,1,1-trimethylolethane, 1,2,6-hexanetriol, 1,2,4-butanetriol, tris(β-hydroxyethyl)isocyanurate, pentaerythritol, mannitol, sorbitol, diethylene glycol, triethylene glycol tetraethylene glycol, dipropylene glycol, polypropylene glycol, polybutylene glycol, xylylene glycol, neopentyl glycol hydroxypivalate and a mixture thereof.

10. A composition as claimed in claim 8, wherein the hydroxy-containing compound as the binder component B) is a polyester polyol formed from a polyhydric alcohol and a polycarboxylic acid or is a polyester polyol formed from a lactone or a hydroxycarboxylic acid.

11. A composition as claimed in claim 8, wherein the hydroxy-containing compound as the binder component B) is a polyurethane polyol.

12. A composition as claimed in any one of claims 1 to 11, which further comprises as a catalyst, an organotin compound in a concentration of from 0.01 to 1% by weight based on the composition.

13. A composition as claimed in any one of claims 1 to 12, which is in the form of particles having a particle diameter of less than 500 μm.

14. A process for producing the composition as defined in any one of claims 1 to 11, which comprises:

homogenizing the components A) and B) in an inert solvent and then removing the solvent, or

homogenizing the components A) and B) in the melt in an extruder or heatable compounder at a temperature not exceeding 180°C.

15. A process as claimed in claim 14, which further comprises grinding the resulting product to form particles having a particle size of less than 500 μm.

16. A method of bonding a heat-resistant substrate, which comprises applying the composition as defined in any one of claims 1 to 13 to a surface of the substrate and curing the composition at a temperature of 150 to 220°C.

17. A method as claimed in claim 16, wherein the substrate is made of a metal.

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